

## Shock temperatures in anorthite glass

Mark B. Boslough<sup>★</sup> and Thomas J. Ahrens *Seismological  
Laboratory, California Institute of Technology, Pasadena, California 91125, USA*

Arthur C. Mitchell *Lawrence Livermore National Laboratory, Livermore,  
California 94550, USA*

Accepted 1985 March 1. Received 1985 February 25; in original form 1984 March 4

**Summary.** Temperatures of  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (anorthite glass) shocked to pressures between 48 and 117 GPa have been measured in the range from 2500 to 5600 K, using optical pyrometry techniques. The pressure dependence of the shock temperatures deviates significantly from predictions based on a single high-pressure phase. Either a variable specific heat, or the existence of three phase transitions, at pressures of about 55, 85 and 100 GPa and with transition energies of about  $0.5 \text{ MJ kg}^{-1}$  each ( $\approx 1.5 \text{ MJ kg}^{-1}$  total) can explain the shock-temperature data. The proposed phase transition at 100 GPa can possibly be identified with the stishovite melting transition. Theoretical models of the time dependence of the thermal radiation from the shocked anorthite based on the geometry of the experiment and the absorptive properties of the shocked material yield good agreement with observations, indicating that it is not necessary to invoke intrinsic time dependences to explain the data in many cases. Observed time dependences were used to calculate absorption coefficients of the shocked material of from about  $2 \text{ mm}^{-1}$  to greater than  $24 \text{ mm}^{-1}$  — an increasing function of shock pressure. The assumption that the shocked material radiates as a black body is supported by the theoretical model, and by the close agreement between measured and calculated black body spectral radiance as a function of wavelength.

**Key words:** anorthite, Hugoniot, optical pyrometry, phase transitions, shock temperature

### Introduction

Because of the cosmochemical abundance of Ca and Al, and the refractory nature of calcium-aluminium silicates such as anorthite, their high-pressure polymorphs are important to consider in any model of the Earth's mantle. Models for the Earth's composition based on

<sup>★</sup> Now at Sandia National Laboratories, Division 1131, Albuquerque, NM 87185, USA.

chondritic abundances predict atomic abundance ratios of  $\text{Ca/Si} \approx 0.05$  and  $\text{Al/Si} \approx 0.07$  (Ross & Aller 1976). It is possible, however, that the lower mantle is significantly enriched relative to the whole Earth in calcium-aluminium silicates, because these are among the first phases to condense from the solar nebula (Grossman & Larimer 1974) and accrete on to the Earth, in inhomogeneous accretion models (Turekian & Clark 1969). Moreover, the construction of equations of state for anorthosite are key ingredients in carrying out cratering calculations for impacts on the crusts of terrestrial planets (Ahrens & O'Keefe 1977, 1983), and in determining quantities of melting and vaporization resulting from such an impact (Boslough & Ahrens 1983).

In previous work on anorthite, a high-pressure equation of state to pressures greater than 120 GPa has been constructed by Jeanloz & Ahrens (1980) based on Hugoniot data only. This equation of state is incomplete in that the thermal behaviour of the shocked material was inferred from pressure–density states only. The parameter which is most sensitive to thermal properties and energetics of phase transitions, namely the temperature, was not measured.

Past work (Kormer *et al.* 1965; Lyzenga, Ahrens & Mitchell 1983; Boslough, Ahrens & Mitchell 1984) has demonstrated the usefulness of shock-temperature data in constraining the high-pressure–high-temperature properties of materials, and in defining phase transitions. For example, the stishovite melting curve was determined from shock-temperature data on  $\alpha$ -quartz and fused quartz. This phase transition is readily apparent from the temperature data, but is not at all obvious from Hugoniot data in the pressure–density plane (Lyzenga *et al.* 1983). It is reasonable to expect similar results for other materials. The purpose of the present study was to measure temperatures of shocked anorthite glass using the optical pyrometry technique, and determine the high-pressure thermal behaviour of  $\text{CaAl}_2\text{Si}_2\text{O}_8$ .

## Experimental

Amorphous  $\text{CaAl}_2\text{Si}_2\text{O}_8$  samples, with measured Archimedeian initial densities of  $2.69 \text{ Mg m}^{-3}$ , were used in these shock-temperature experiments. The samples, obtained from Corning Glass Co. (Corning, New York), were clear and homogeneous, with a composition described by  $\text{An}_{99.5}\text{Ab}_{0.4}\text{Or}_{0.1}$  – essentially the composition of pure anorthite. A microprobe analysis of a representative sample is given in terms of oxides in Table 1. The transmittance of a 3 mm thick, polished sample of the glass over the wavelength range of interest is shown in Fig. 1, measured with a Cary Model 17 spectrophotometer.

**Table 1.** Electron microprobe analysis of anorthite glass (Corning).

Oxide	Wt (per cent)
$\text{Na}_2\text{O}$	0.05
$\text{MgO}$	0.00
$\text{Al}_2\text{O}_3$	36.36
$\text{SiO}_2$	43.48
$\text{K}_2\text{O}$	0.01
$\text{CaO}$	20.73
$\text{TiO}_2$	0.06
$\text{FeO}$	0.04
$\text{BaO}$	0.03
Total	100.76

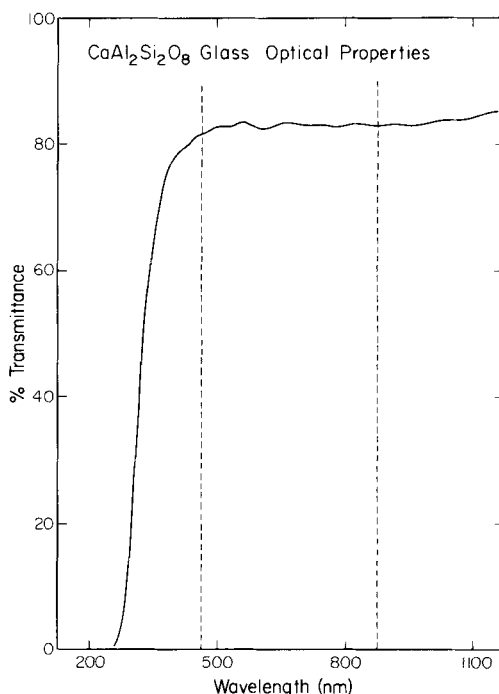


Figure 1. Transmittance spectrum of a representative sample of  $\text{CaAl}_2\text{Si}_2\text{O}_8$  glass (sample An7T), measured by Cary 17 spectrophotometer. Transmittance shows negligible wavelength dependence between wavelength limits of optical pyrometers (dashed lines).

Shock experiments were carried out on two-stage light-gas guns at the California Institute of Technology and Lawrence Livermore National Laboratory. Copper and tantalum projectiles were accelerated to velocities between 3.7 and 5.7  $\text{km s}^{-1}$ . Projectile velocities were determined using flash X-radiography, as described elsewhere (Jeanloz & Ahrens 1977; Mitchell & Nellis 1981a). Shock pressures were determined by the method of impedance matching (Rice, McQueen & Walsh 1958) and using the standard equations of state of Mitchell & Nellis (1981b) for tantalum and copper, and the Hugoniot of Boslough, Rigden & Ahrens (1986), for the anorthite glass.

Temperatures were determined by measuring the intensity of thermally radiated light at several wavelengths in the visible and near-infrared wavelengths. The thermal radiation was filtered by interference filters and focused on to silicon photodiodes. The resulting electrical signals were recorded by an array of oscilloscopes with Polaroid cameras. The recorded time-resolved voltages are directly proportional to the spectral radiances of the thermal radiation. Calibration of the pyrometer system was carried out using light sources with known spectral radiances in the wavelength range in which measurements were made. The two optical pyrometers used in this study are described in detail by Lyzenga & Ahrens (1979) and Boslough (1983).

## Results

Eight shock-temperature experiments were conducted on anorthite glass; three (An1T, An2T and An3T) using a 10 nm bandwidth six-channel optical pyrometer at Lawrence Livermore National Laboratory (Lyzenga & Ahrens 1979), and five (An5T–An10T) using a

40 nm bandwidth four-channel optical pyrometer at the California Institute of Technology (Boslough 1983). Representative data are shown in Figs 2 and 3.

Three general types of time dependence were observed. In shots An6T, An5T and An3T – the three experiments below 70 GPa – the sharp increase in intensity corresponding to the entrance of the shock wave into the sample is followed by an exponential decay to an approximately constant value (Fig. 2a). In shots An2T, An7T, An1T and An10T – four experiments above 90 GPa – the light intensity remains constant to within about 10 per cent until the shock wave reaches the free surface or is overtaken by an edge rarefaction (Fig. 2b). Shot An9T – to about 85 GPa – shows an anomalous behaviour, in which the intensity decreases at a non-uniform rate during shock transit (Fig. 3).

There are three causes which could account for time dependence in the emitted light: temperature dependence, emissivity dependences, or time dependence of the absorption or scattering of an intervening layer. All three of these causes are invoked to explain the observed time dependences. It is important to note that the observed light is not necessarily radiated from only the shock front unless the shocked material is perfectly opaque. In general, a material that is initially semi-transparent, with initial linear absorption coefficient  $a_u$  is shocked to a state with linear absorption coefficient  $a_s$  and temperature  $T$ . The absorbance of the unshocked layer is

$$A_u = 1 - \exp(-a_u d_u)$$

and the shocked layer is

$$A_s = 1 - \exp(-a_s d_s)$$

where  $d_u$  and  $d_s$  are the thicknesses of unshocked and shocked layers, respectively. According to Kirchhoff's radiation law for a non-reflector (Jenkins & White 1976) the emissivity of a layer is equal to its absorbance. If the sample thickness is  $d$ , the shock velocity is  $U_s$ , the velocity of the shocked material (particle velocity) is  $u_p$ , and grey body light (with a Planckian wavelength distribution and an emissivity less than unity) is radiated only from the shocked layer at constant temperature  $T$ , the time dependence of observed light intensity from the shocked layer at a given wavelength will be

$$I_s(t) = f(T) \{1 - \exp[-a_s(U_s - u_p)t]\} \exp[-a_u(d - U_s t)], \quad (1)$$

where  $f(T)$  is the Planck distribution function, and  $t$  is the time after impact. In the case of anorthite glass, the initial state is essentially transparent (Fig. 1), so  $a_u = 0$  and this becomes:

$$I_s(t) = f(T) \{1 - \exp[-a_s(U_s - u_p)t]\}. \quad (2)$$

It is also necessary to consider the effect of light generated at the interface between the driver and sample material, due to the non-ideality of the surfaces, which, despite their optical quality, have imperfections which leave a gap on the order of 1  $\mu\text{m}$  wide as determined by counting visible fringes (Newton rings) with an optical flat.

The temperature at the interface due to passage of the shock wave is higher than the shock temperature of either boundary material, due to multiple reverberation (Urtiew & Grover 1974) and shock heating of any gas trapped in the gap. The temperature decay as a function of time at the interface can be modelled simply as a Fourier diffusion boundary value problem in one dimension. The metallic driver is considered to be a thermally conducting half-space with initial temperature  $T_d$ , the shock temperature of the driver, and thermal diffusivity  $\kappa$ . The sample is modelled as a thermal insulator. This problem is solved by

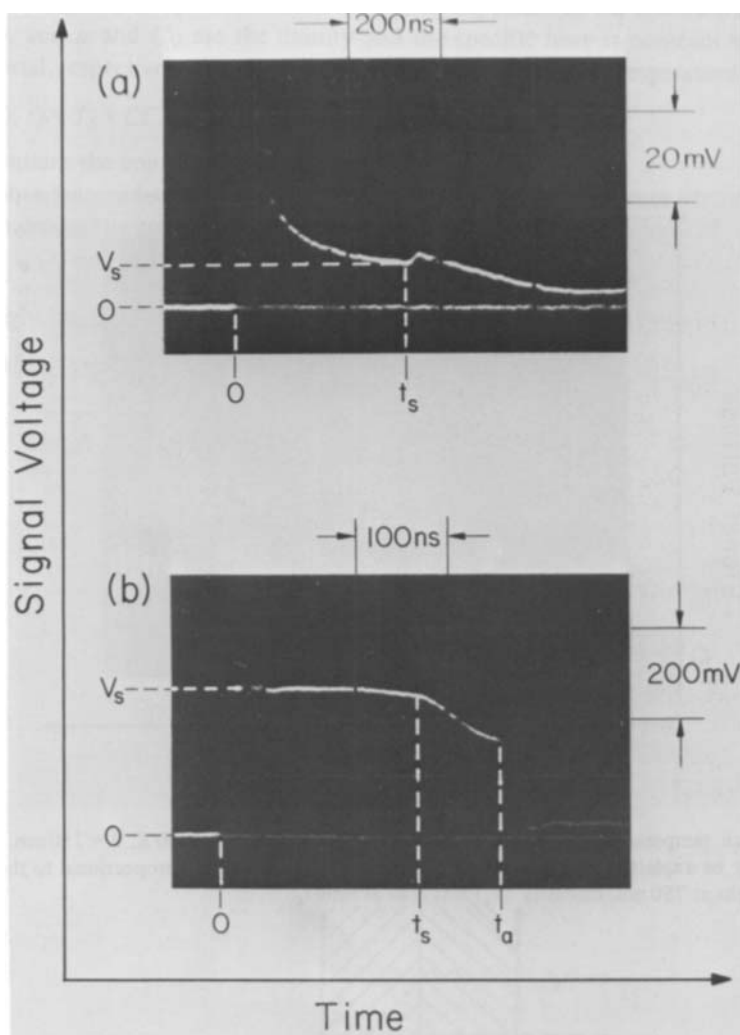


Figure 2. Shock temperature records for  $\text{CaAl}_2\text{Si}_2\text{O}_8$  glass. Signal voltage is directly proportional to the intensity of the radiated light at the wavelength of the filter. (a) An5T:  $P = 55 \text{ GPa}$ ,  $T = 2700 \text{ K}$ ,  $\lambda = 750 \text{ nm}$ . Time dependence is due to a combination of effects: cooling of interface and thickening of radiating (shocked) layer. (b) An10T:  $P = 117 \text{ GPa}$ ,  $T = 5600 \text{ K}$ ,  $\lambda = 600 \text{ nm}$ . Initially constant signal due to high opacity of shocked layer. Decrease in intensity just before free surface arrival time ( $t_a$ ) due to decay of shock by edge rarefaction. Intensity ( $V_s$ ) was read at time  $t_s$ .

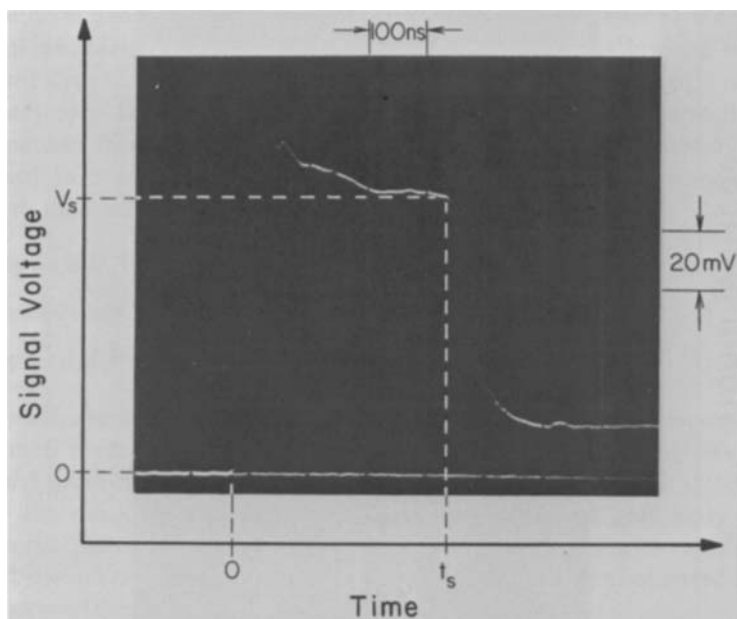


Figure 3. Shock temperature record for shot An9T:  $P = 85$  GPa,  $T = 4000$  K,  $\lambda = 750$  nm. Time dependence can only be explained by unsteady shock. Signal voltage is directly proportional to the intensity of the radiated light at 750 nm. Intensity ( $V_s$ ) was read at time  $t_s$ .

Carslaw & Jaeger (1959, p. 51). The solution is

$$T(x, t) = T_d + \frac{Q}{2\rho C_V \sqrt{\pi \kappa t}} \exp(-x^2/4\kappa t), \quad (3)$$

where  $t$  is the time after impact,  $x$  is the distance of a point in the driver from the interface,  $Q$  is the quantity of heat per unit area (unknown) deposited at the interface by the closing of the gap, and  $\rho$  and  $C_V$  are the density and the specific heat at constant volume of the driver material, respectively. The time dependence of the interface temperature is

$$T_i(t) = T(0, t) = T_d + Ct^{-1/2}, \quad (4)$$

where  $C$  contains the constants from equation (3).

If the interface radiates as a black body, the observed light intensity from it (with attenuation due to the growing shocked layer) is

$$I_i(t) = f(T_d + Ct^{-1/2}) \exp[-a_s(U_s - u_p)t]. \quad (5)$$

The total light intensity observed is due to both sources (equations (2) and (5))

$$I(t) = f(T) [1 - \exp[-a_s(U_s - u_p)t]] + f(T_d + Ct^{-1/2}) \exp[-a_s(U_s - u_p)t]. \quad (6)$$

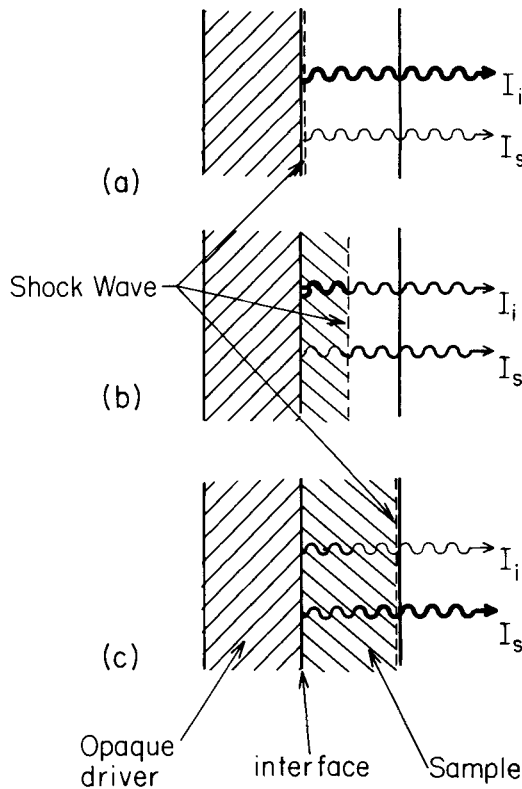


Figure 4. Schematic of shock temperature experiment. Measured light intensity is sum of light from interface ( $I_i$ ) and shocked sample layer ( $I_s$ ). (a) Just after shock enters sample, light from hot interface dominates, and is not attenuated significantly by thin shocked layer. (b)  $I_i$  has decreased due to cooling of interface and thickening of attenuating layer.  $I_s$  has increased due to thickening of emitting layer. (c) Interface has cooled and is further blocked by thick shocked layer.  $I_s$ , the light intensity characteristic of the shock temperature, now dominates.

One can easily see that for  $t \gg 1/a_s(U_s - u_p)$ , the shocked layer is effectively an opaque black body, and there is no time dependence in the observed intensity. For sufficiently large  $a_s$ , this occurs at  $t$  smaller than the rise time of the pyrometer photodiode and no time-dependent behaviour is observed at all. This is observed in shots An1T, An7T and An10T (Fig. 2b).

For smaller  $a_s$ , the time dependence is depicted schematically in Fig. 4, and is illustrated by the spectral radiance observed in shot An3T in Fig. 5. The contribution due to the shocked sample increases from zero, when the shock wave enters the sample, asymptotically to  $f(T)$ , the intensity of a black body at temperature  $T$ , with a time constant  $\tau = 1/a_s(U_s - u_p)$ . The interface contribution decreases from infinity (because of the idealized assumption that all the heat is deposited at the two-dimensional interface) to zero, with a time constant  $\tau < 1/a_s(U_s - u_p)$ , because the source is also decaying with time. The observed light intensity is the sum which decreases asymptotically to  $f(T)$ , with an effective decay time bounded above by  $1/a_s(U_s - u_p)$ . This is the time dependence observed in shots An2T, An3T, An5T and An6T (Fig. 2a).

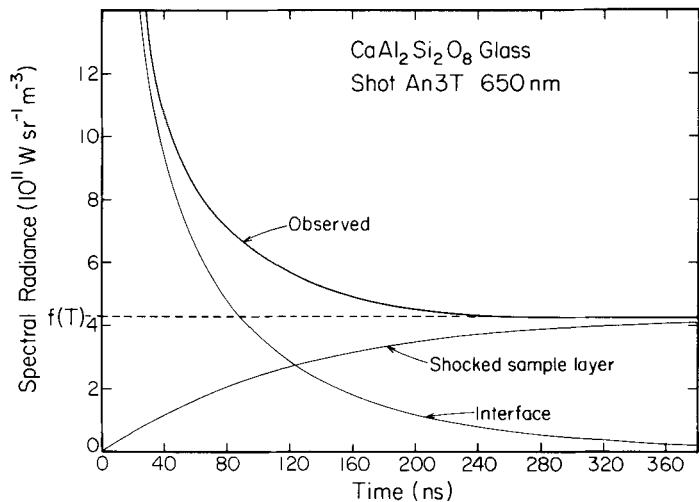


Figure 5. Measured spectral radiance from shot An3T ( $P = 66$  GPa,  $T = 3000$  K) at  $\lambda = 650$  nm. The measured time dependence can be fitted by a function of the form:  $A [1 - \exp(-\alpha t)] + B t^{-1/2} \exp(-\alpha t)$ , an approximation of equation (6), with  $A = 4.3 \times 10^{11} \text{ W Sr}^{-1} \text{ m}^{-3}$ ,  $B = 8.2 \times 10^{12} \text{ W Sr}^{-1} \text{ m}^{-3}$ , and  $\alpha = 8.0 \times 10^{-3} \text{ ns}^{-1}$ .

Table 2. Bounds on absorptivity of shocked anorthite glass.

Shot	$\tau$ ( $\mu\text{s}$ )	$U_s - u_p$ ( $\text{mm } \mu\text{s}^{-1}$ )	$a_s \text{ max}$ ( $\text{mm}^{-1}$ )	Pressure (GPa)
An6T	0.15	3.8	1.8	48.5
An5T	0.10	4.1	2.4	55.3
An3T	0.08	4.5	2.8	66.6
An2T	0.01	4.7	21.0	84.6
Others	<0.007	<6.0	>24.0	>90.0

$$a_s \text{ max} = \frac{1}{\tau (U_s - u_p)}$$



One experiment, An9T, exhibits time-dependent behaviour not accounted for by this simple model. The intensity of the emitted light decreases in steps as the shock wave passes through the sample, indicating that the time dependence is in the shock front itself, as a fluctuation in temperature, absorption coefficient, or both. This is similar to behaviour observed in fused quartz shocked to the stishovite-liquid mixed phases region by Lyzenga *et al.* (1983), which they interpret as a possible rate-dependent behaviour due to metastability near the phase transition pressure.

In the simple model developed above (equation 6), the linear absorption coefficient  $a_s$  for the shocked anorthite can be constrained by measuring the effective decay times from the oscilloscope records for the shots whose results agree with the model. The upper bound for  $a_s$  is  $a_{s \max} = 1/\tau(U_s - u_p)$ . These values are tabulated in Table 2. The bound on  $a_s$  is seen to be an increasing function of shock pressure.

### CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> shock temperatures

Temperatures were calculated from the spectral radiance data by fitting them to a Planck function, as outlined by Boslough (1983) and Boslough *et al.* (1984). This was done in two ways for each experiment. First, a least squares fit is carried out in which both the temperature  $T$  and emissivity  $\epsilon$  are independent variables. The temperatures and emissivities determined in this manner are given in Table 3, along with the standard deviation  $\sigma$  and the mean fractional deviation  $\sigma/\bar{N}_\lambda$  of the fit (where  $\bar{N}_\lambda$  is the mean measured spectral radiance). There appears to be no correlation between the shock pressure and the emissivity which gives the best fit, and in the majority of cases the best-fitting emissivity is greater than unity – an unphysical situation.

It should be noted here that disregarding the emissivities obtained using a two parameter least squares fit is not without justification. The Planck function at a given wavelength,  $\lambda$ , is

$$f(\epsilon, T) = \epsilon C_1 \lambda^{-5} [\exp(C_2/\lambda T) - 1]^{-1}, \quad (7)$$

where  $C_1$  and  $C_2$  are constants. One can easily see that this function is strongly dependent on  $T$ , particularly in the low  $\lambda T$  limit, where the dependence is exponential. The  $\epsilon$  dependence, however, is linear. When the function is inverted for the fit,  $\epsilon$  is a much more sensitive function of the measured spectral radiance than is  $T$ . Small errors in the measured spectral radiance therefore weigh much more heavily on  $\epsilon$  than on  $T$ , particularly when these two variables are balanced against each other as they are in a two parameter fit. Because of this discrepancy, and the fact that the model developed in the previous section implies that the observed intensity corresponds to a black body on the asymptote, temperatures were also calculated assuming  $\epsilon = 1.0$ , and conducting a standard single variable least squares fit for  $T$ .

In the two parameter fit for four of the eight anorthite shots, the best-fitting emissivities are within 10 per cent of unity, and the goodness of the fits, as determined by the standard deviations, are not significantly reduced by requiring that  $\epsilon = 1.0$ . In three shots, the best-fitting emissivities are significantly greater than unity. Two of these shots, An2T and An6T, have extremely good fits, with mean fractional standard deviations of 0.01 and 0.02, respectively. However, the emissivities which give rise to these fits are 1.34 and 1.76, respectively; unphysical values which imply that the quality of the fits is fortuitous. When the inversion is carried out with an emissivity of unity for these three shots, however, the qualities of the fits are still comparable to those for the other experiments.

In one shot (An7T), spectral radiance data was obtained at only one wavelength. The shock temperature of this shot was assumed to be the brightness temperature. This assumption is based on the close agreement between the observed spectral radiances and black body

Table 3. Anorthite glass shock-temperature data.

Shot	Flyer/ driver material	Projectile velocity (km s <sup>-1</sup> )	Initial density (Mg m <sup>-3</sup> )	Pres- sure <sup>(d)</sup> (GPa)	Temperature calculation				
					Method	$\epsilon$	$T$ (K)	$\sigma$ (W Sr <sup>-1</sup> m <sup>-3</sup> )	$\sigma/\bar{N}\lambda$
An6T (LGG132)	Cu/Cu	3.72 ± 0.10	2.6908 ± 0.0010	48.5 ± 2.1	(a)	1.76	2323 ± 5	0.2 × 10 <sup>10</sup>	0.02
					(b)	1.00	2481 ± 37	1.4 × 10 <sup>10</sup>	0.13
An5T (LGG131)	Cu/Cu	4.038 ± 0.002	2.6909 ± 0.0013	55.3 ± 1.1	(a)	0.98	2723 ± 37	2.7 × 10 <sup>10</sup>	0.12
					(b)	1.00	2714 ± 39	2.8 × 10 <sup>10</sup>	0.12
An3T (LLL091880)	Cu/Cu	4.536 ± 0.006	2.6900 ± 0.0010	66.6 ± 1.2	(a)	1.05	2997 ± 104	1.5 × 10 <sup>11</sup>	0.30
					(b)	1.00	3017 ± 105	1.5 × 10 <sup>11</sup>	0.30
An9T (LGG138)	Cu/Cu	5.255 ± 0.003	2.6953 ± 0.0012	84.6 ± 1.3	(a)	1.01	4002 ± 21	1.2 × 10 <sup>11</sup>	0.03
					(b)	1.00	4010 ± 22	1.3 × 10 <sup>11</sup>	0.04
An2T (LLL091680)	Cu/Cu	5.455 ± 0.010	2.6899 ± 0.0011	90.0 ± 1.3	(a)	1.34	3802 ± 6	0.4 × 10 <sup>11</sup>	0.01
					(b)	1.00	3985 ± 71	4.0 × 10 <sup>11</sup>	0.12
An7T (LGG137)	Cu/Cu	5.563 ± 0.006	2.6927 ± 0.0011	92.9 ± 1.2	(c)	1.00	4564 ± 104		
An1T (LLL062380)	Ta/Ta	5.678 ± 0.010	2.6893 ± 0.0011	111.4 ± 1.3	(a)	1.24	4904 ± 76	1.1 × 10 <sup>12</sup>	0.08
					(b)	1.00	5110 ± 122	1.6 × 10 <sup>12</sup>	0.12
An10T (LGG139)	Ta/Cu	5.562 ± 0.003	2.6944 ± 0.0012	117.6 ± 1.1	(a)	0.91	5741 ± 218	3.5 × 10 <sup>12</sup>	0.19
					(b)	1.00	5625 ± 214	3.6 × 10 <sup>12</sup>	0.20

- (a) Best fit with Planck function and variable  $\epsilon$ .  
 (b) Best fit with Planck function and  $\epsilon \equiv 1$  (black body).  
 (c) Brightness temperature.  
 (d) Determined by impedance matching.

distributions in the other seven experiments. The temperature error for this shot was taken from the estimated error in the measured spectral radiance.

In the other seven shots, the temperature errors were determined systematically by the equation

$$\Delta T = \frac{\sigma_N}{f_T(T, \lambda = 600 \text{ nm})}, \quad (8)$$

where  $\sigma_N$  is the standard deviation in spectral radiance, and  $f_T(T, \lambda)$  is the partial derivative of the Planck distribution function with respect to temperature. The partial derivative was evaluated at a wavelength of 600 nm, because this is near the middle of the widest wavelength range used.

The intensities used in the temperature calculations were taken from the oscilloscope

records as indicated in Figs 2 and 3. According to the simple model, the intensity of light most representative of thermal radiation from the shocked region of the sample is just before the shock wave arrives at the free surface. In all but one case, that is where the oscillograms were read. In the other case, shot An9T, the shock wave begins to decay before it approaches the free surface, apparently due to an edge rarefaction. The intensity was taken from this set of shot records just prior to the beginning of the decay of the shock wave. The spectral radiances determined in this manner are tabulated in Tables 4 and 5. Plots which

**Table 4.** Anorthite glass spectral radiance data for shots carried out using LLNL pyrometer.

$\lambda^{(1)}$	An1T $N_{\lambda}^{(2)}$	An2T $N_{\lambda}$	An3T $N_{\lambda}$
450.2	$11.4 \pm 0.6$	$1.92 \pm 0.15$	$0.109 \pm 0.070$
507.9	$13.3 \pm 0.5$	$2.73 \pm 0.29$	$0.327 \pm 0.049$
545.1	$14.9 \pm 0.8$	$3.24 \pm 0.13$	$0.489 \pm 0.094$
598.0	$14.3 \pm 0.4$	$3.72 \pm 0.23$	$0.433 \pm 0.044$
650.0	$14.5 \pm 0.7$	$4.09 \pm 0.21$	$0.670 \pm 0.123$
792.0	$11.5 \pm 0.3$	$4.34 \pm 0.32$	$0.951 \pm 0.044$

(1) Wavelength ( $\lambda$ ) in nm.

(2) Spectral radiance ( $N_{\lambda}$ ) in  $10^{12} \text{ W m}^{-3} \text{ Sr}^{-1}$ .

**Table 5.** Anorthite glass spectral radiance data for shots carried out using Caltech pyrometer.

An5T		An6T		An7T		An9T		An10T	
$\lambda^{(1)}$	$N_{\lambda}^{(2)}$	$\lambda$	$N_{\lambda}$	$\lambda$	$N_{\lambda}$	$\lambda$	$N_{\lambda}$	$\lambda$	$N_{\lambda}$
454.4	$0.0455$ $\pm 0.0078$	454.8	$0.0137$ $\pm 0.0076$	Off scale		453.5	$2.18$ $\pm 0.09$	453.0	$23.5$ $\pm 1.2$
556.8	$0.165$ $\pm 0.014$	557.2	$0.0595$ $\pm 0.0105$	Off scale		603.2	$3.98$ $\pm 0.14$	602.8	$19.0$ $\pm 0.7$
647.6	$0.314$ $\pm 0.028$	647.6	$0.0128$ $\pm 0.019$	Off scale		747.5	$4.25$ $\pm 0.15$	747.3	$19.0$ $\pm 1.6$
748.3	$0.412$ $\pm 0.036$	748.4	$0.0228$ $\pm 0.024$	903.3	$0.623$ $\pm 0.026$	903.3	$3.77$ $\pm 0.17$	903.3	$11.9$ $\pm 0.5$

(1) Wavelength ( $\lambda$ ) in nm.

(2) Spectral radiance ( $N_{\lambda}$ ) in  $10^{12} \text{ W m}^{-3} \text{ Sr}^{-1}$ .

show the measured spectral radiances and those calculated for the black body temperatures which give the best fits are illustrated in Figs 6 and 7.

Temperatures determined by both of these methods, along with their respective emissivities, standard deviations in spectral radiance and fractional standard deviations, are summarized in Table 3. The associated pressures are determined from the measured projectile velocity, and impedance matching with a fit to the  $U_s - u_p$  data obtained in the Hugoniot experiments on anorthite glass (Boslough *et al.* 1986). These impedance-match determined pressures are the preferred values to use when modelling the pressure-temperature Hugoniot, despite the fact that pressures were determined more directly for each shot by measuring shock-transit times. In the more direct pressure determination, projectile and shock velocity must both be measured. The precision by which the shock velocity can be measured

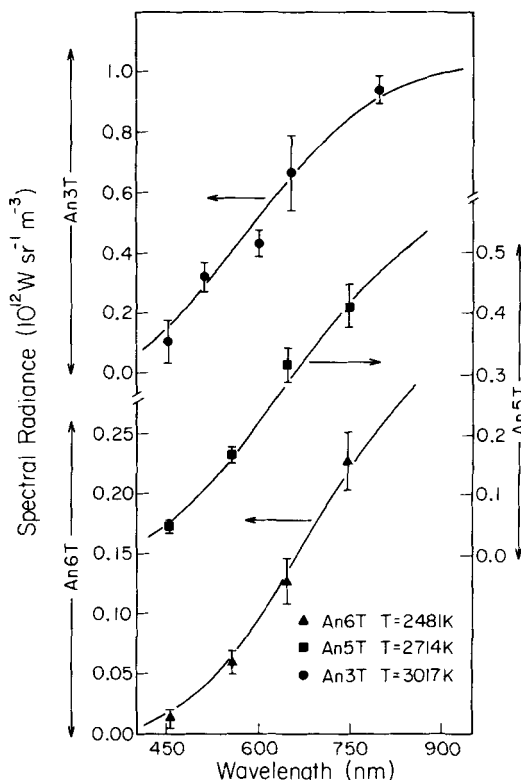


Figure 6. Spectral radiances measured in shots An6T, An5T and An3T with best fitting black body curves.

is not as high as that of the projectile velocity measurement, and larger random errors can be introduced. In the impedance-match method, only the projectile velocity is used, which can be measured to better than  $\pm 0.2$  per cent, and a curve which is determined by a least-squares fit to the direct pressure measurements. This in effect smooths out the random errors.

## Discussion

The measured shock temperatures in anorthite glass are plotted as a function of Hugoniot pressure in Fig. 8, along with pressure-temperature Hugoniot calculations based on several models. These models are the Jeanloz & Ahrens (1980) equation of state with a Dulong–Petit specific heat ( $C_V = 3R$ ), the same equation of state with variable specific heat, and a model in which several phase transitions occur. The latter two models can provide reasonable fits to the data. The method of Ahrens, Anderson & Ringwood (1969) was used to calculate shock temperatures in all cases.

The Jeanloz & Ahrens equation of state considers all states above 30 GPa on the Hugoniot of anorthite crystal to be a single high pressure phase, as found by McQueen, Marsh & Fritz (1967), and fits the Hugoniot data with a third-order Eulerian finite strain (Birch–Murnaghan) isentrope (Davies 1973). The Gruneisen parameter was calculated by the pressure offset of the porous Hugoniot. The transition energy between single crystal anorthite and the metastable high pressure phase at standard conditions ( $E_{tr}$ ) in this equation of state is  $0.72 \text{ MJ kg}^{-1}$ . This corresponds to an  $E_{tr}$  of  $0.46 \text{ MJ kg}^{-1}$  for anorthite

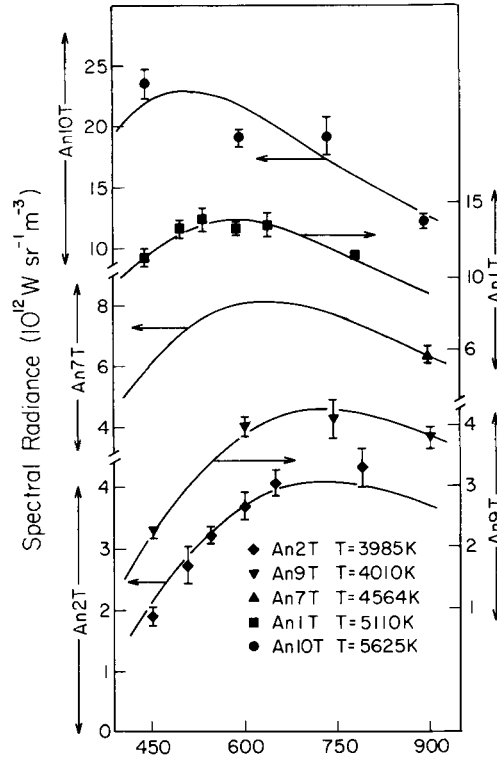


Figure 7. Spectral radiances measured in shots An2T, An9T, An7T, An1T and An10T with best fitting black body curves.

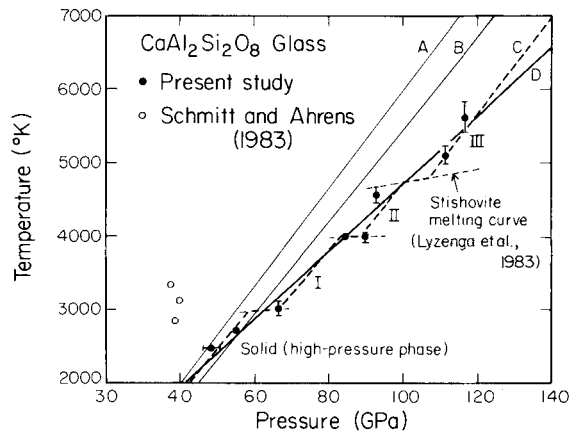


Figure 8. Measured shock temperatures of  $\text{CaAl}_2\text{Si}_2\text{O}_8$  assuming  $\epsilon = 1.0$ , and four calculated pressure-temperature Hugoniot. (a) Mixed oxide model of Boslough *et al.* (1986). (b) Jeanloz & Ahrens (1980). (c) This study, assuming three phase transitions to high-pressure phase regimes denoted by I, II and III and  $C_V = 3R$ . (d) This study, assuming no phase transitions and  $C_V = A + BT$ . The lower two dashed lines are hypothetical phase transitions. The upper one is the stishovite melting curve (Lyzenga *et al.* 1983). Three shock temperature data by Schmitt & Ahrens (1983) are included, which exhibit heterogeneous hot spot (grey body) behaviour.

glass, when the  $0.26 \text{ MJ kg}^{-1}$  energy difference between anorthite glass and single crystal is accounted for (Robie, Hemingway & Fisher 1978). Jeanloz & Ahrens (1980) considered anorthite above 2000 K to be a Debye solid in the classical limit — anorthite having a Debye temperature of 1000 K — and used the Dulong–Petit specific heat. This calculation gives reasonable agreement to the measured points below 60 GPa, but overestimates the shock temperature at higher pressure by as much as 1000 K. Clearly, the slope described by the data is less steep than the calculated slope.

In calculating shock temperatures by the method of Ahrens *et al.* (1969), the only way the theoretical  $T$ – $P$  slope can change is to have a pressure- or temperature-dependent  $C_V$  and/or phase transitions. There is ample theoretical and experimental evidence for a temperature-dependent  $C_V$  in this temperature range, in departure from the Debye model of solids. A specific heat of the form

$$C_V = A + BT \quad (9)$$

is given by Wallace (1972), where  $A = 3R$  and  $B = \Gamma_2 - 2A_2$ . Here,  $\Gamma_2$  is the electronic contribution and  $A_2$  is the first-order anharmonic lattice contribution. The same form has been shown by Lyzenga *et al.* (1983) to describe shock temperature dependence on pressure for solid and liquid stishovite.

The coefficients for the best fit to the anorthite data are  $A = 0.92 \text{ kJ kg}^{-1} \text{ K}^{-1}$  (21 per cent less than the Dulong–Petit value,  $3R = 1.17 \text{ kJ kg}^{-1} \text{ K}^{-1}$ ) and  $B = 9.3 \times 10^{-5} \text{ kJ kg}^{-1} \text{ K}^{-2}$ . These coefficients are comparable to those determined by Lyzenga *et al.* (1983) for solid and liquid stishovite, which has approximately the same mean atomic weight per atom as anorthite, with mean values of  $A = 0.86 \text{ kJ kg}^{-1} \text{ K}^{-1}$  and  $B = 1.17 \times 10^{-4} \text{ kJ kg}^{-1} \text{ K}^{-2}$ .  $B$  is in fact smaller for all the anorthite data taken together than for the single phases of the  $\text{SiO}_2$  data, which indicates less temperature dependence for  $C_V$  overall.

It is probably unreasonable to expect that the anorthite undergoes no phase transition above 50 GPa on its Hugoniot when one considers the complexity of its phase diagram below 30 GPa (Liu 1978), and when the behaviour of a simpler silicate,  $\text{SiO}_2$ , is considered in the same pressure range (Lyzenga *et al.* 1983). Anorthite disproportionates to grossular, kyanite, and quartz at pressure from 3 to 15 GPa (Goldsmith 1980; Boyd & England 1961) and at 15 GPa the quartz transforms to stishovite along its Hugoniot (McQueen, Fritz & Marsh 1963). Phase changes in grossular have been observed above 25 GPa (Liu 1979). Hugoniot data indicate a mixed phase region in anorthite from 10 to 33 GPa (Jeanloz & Ahrens 1980). Jeanloz & Ahrens (1980) give four candidate high-pressure phases above 33 GPa:  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (hollandite),  $\text{CaO}$  (B2 structure) +  $\text{Al}_2\text{O}_3$  (corundum) +  $2\text{SiO}_2$  (stishovite) — (mixed oxide assemblage),  $\text{CaAl}_2\text{O}_4$  (calcium ferrite structure) +  $\text{SiO}_2$  (stishovite), and  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  (sodium titanate structure) +  $\text{Al}_2\text{O}_3$  (corundum) +  $3\text{SiO}_2$  (stishovite). It is not unlikely, however, that phase transitions occur between these candidate phases, or others, above 33 GPa, or that further disproportionations or polymorphic transitions occur in the components of the candidate assemblages. Melting is also expected to occur in this shock-pressure range.

With each phase change is associated an energy of transition, which can be expressed in terms of  $\Delta E_{\text{tr}}$ , the energy difference between the metastable phases at standard conditions. The measured temperature for anorthite shocked into a mixed phase region will, if in equilibrium, lie on the coexistence curve. For anorthite shocked into a single phase regime, the measured temperature will lie  $\Delta E_{\text{tr}}/C_V$  below the calculated metastable temperature of the lower phases. The slopes of the single-phase segments of the Hugoniot depend on  $C_V$  for that phase.

For constant  $C_V = 3R$ , at least three phase transitions (to assemblages indicated as I, II and III in Fig. 8) are required to give a good fit to the data. If stishovite is a component of

assemblage II, the highest transition – at about 4800 K – may correspond to the stishovite melting coexistence curve determined by Lyzenga *et al.* (1983) who found  $\Delta E_{\text{tr}}$  for the stishovite to liquid transition to be about  $1.6 \text{ MJ kg}^{-1}$ . The transition at 4800 K in anorthite gives a temperature difference of about 450 K between the phases, which leads to  $\Delta E_{\text{tr}} \approx 0.5 \text{ MJ kg}^{-1}$ . The mass fraction of  $\text{SiO}_2$  in  $\text{CaAl}_2\text{Si}_2\text{O}_8$  is about 0.36, so if this phase transition is melting of  $\text{SiO}_2$  only, this  $\Delta E_{\text{tr}}$  corresponds to  $1.4 \text{ MJ kg}^{-1}$  in the  $\text{SiO}_2$ , which compares well with the  $1.58 \text{ MJ kg}^{-1}$  value of Lyzenga *et al.* (1983).

## Conclusions

When shock-temperature data are included in the description of the high-pressure phase assemblages in the system  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , its behaviour may be too complicated to be described by a single high-pressure phase equation of state such as Jeanloz & Ahrens (1980). Although the shock-temperature data can be roughly approximated assuming a single phase and choosing a temperature-dependent model for  $C_V$ , the average scatter of data around the best such single-phase curve in the pressure-temperature plane is still greater than the estimated errors in the temperature measurements. It is also reasonable to interpret the shock-temperature data by assuming that a series of phase transitions continue to occur along the Hugoniot. The data are consistent with three phase transitions – at about 55, 85 and 100 GPa – each with a transition energy of about  $0.5 \text{ MJ kg}^{-1}$ . The exact transition energies and pressures are not, however, well constrained by the data. The most realistic model would include both a temperature-dependent  $C_V$  and phase transitions. It is also possible that when melting does occur, it does so incongruently, with a compositional difference between the melt and solid. Such a transition must be treated in the context of a multi-component system, in contrast to the stishovite melting transition, for which  $\text{SiO}_2$  can be treated as a single-component system. A possible consequence of incongruent melting would be a smearing out of discontinuities and spreading of the mixed phase region out over a larger pressure range, and a resulting shallow slope for the Hugoniot in the pressure–temperature plane.

Success of modelling the time dependence of the measured spectral radiances demonstrates the potential usefulness of the optical pyrometry method in studying optical properties of shocked material in addition to measuring shock temperatures. By taking advantage of this fact the decay times of emitted light can be used to determine the absorption coefficient of the material behind the shock front, as in the case of anorthite glass, for which the absorption coefficient increases from about  $2 \text{ mm}^{-1}$  to greater than  $24 \text{ mm}^{-1}$  as a function of shock pressure (Table 2). Future experiments can be designed to determine absorption coefficient as a function of shock pressure, and the shock state can be further characterized in this way.

## Acknowledgments

We are indebted to E. Gelle, M. Long, and C. Manning of the Caltech Shock Wave Laboratory, and to D. Bakker, E. Jerbic and others at the Livermore facility for their expert technical help. We are grateful for the helpful discussions with G. Lyzenga, W. Nellis and J. Trainor. We wish to thank G. Rossman and his students at Caltech, who assisted in the determination of optical properties. Support was provided by NSF EAR7812942 and NASA NGL-



05-002-105 at the California Institute of Technology, and by the Lawrence Livermore National Laboratory. Contribution 3932, Division of Geological and Planetary Sciences, California Institute of Technology.

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